CHARACTERIZATION OF INTERPHASES BY NANOMECHANICAL MAPPING AND CORRELATION WITH MACROSCOPIC MECHANICAL PROPERTIES

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Abstract
Uni-directional glass fibre/epoxy composites with very high volume fractions have been elaborated and characterized. The aim of the study is to correlate different scales of characterization to improve our understanding of such materials behavior which should help in their design. The composite is analyzed at nanometric scale by a nanomechanical property mapping Atomic Force Microscope (PEAKFORCE QNM). Modulus images are simultaneously obtained with adhesion and deformation images of interfacial areas. Two different interphases are identified; a rigid one close to fibre surface and a softer one up to several hundred nanometers from fibre surface. Nanoscale measurements are then correlated with static macroscopic measurements and Dynamic Mechanical Analysis performed on the same UD composites in transverse mode.

1. Introduction

The interfacial area between the matrix and reinforcement strongly influence the mechanical properties at initial state and its durability in service life. The characterization of this area requires specific techniques operating at sub-micron scale [1, 2]. Nanoindentation tests have been used in the last decade to characterize the interphases in organic matrix composites [3-9]. It often generates artifacts due to boundary effects close to fibre surface. The consequences are that interphases systematically appear more rigid than the matrix with these methods. Other methods rather show opposite properties attributed to an incomplete curing [10,11] or to plasticizing effects resulting from fibre silane treatment [12-14]. At higher scale, Dynamic Mechanical analysis may also bring useful information on global matrix mobility and its modifications due to fibre introduction for example [7,15,16]. The main relaxation peak sometimes present shoulders at lower or higher temperatures than Tα, attributed to network crosslinking heterogeneities [17, 18]. Static mechanical tests, especially in transverse mode characterize the interfacial strength which influences the composite toughness [3, 17] and fatigue life [19]. The aim of the present study is to validate a new method to characterize interfacial areas at nanometre scale and to correlate its properties with usual mechanical properties determined at macro-scale.

2. Materials and testing methods

The uni-directional composites are made with a commercial epoxy matrix reinforced with 70 % (±2%) mass fraction of glass fibres treated with a commercial sizing.
The matrix/fibre interfacial strength is determined by a three-point bending test in transverse mode performed on a MTS DY35 universal tensile equipment. The samples of 40x15x2 mm3 were cut with a diamond saw in transverse direction for the composite. A constant crosshead speed of 1mm/min was

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used according to the standard NF EN 2746 and the force-displacement curves were analyzed with MTS TestWorks® 4 software. Each value is an average of five measurements.
The viscoelastic behaviour of the bulk resin and the composite was studied by dynamic mechanical analysis using a DMA Q800 from TA Instruments. Samples sizes of 40x10x2 mm^3 were cut with a diamond saw. The samples were tested in single cantilever mode in transverse direction with 7 µm amplitude at 1Hz. A heating rate of 2 °C/min was applied between 30°C and 180 °C. The deconvolution of the relaxation curves was performed by ORIGIN 8 software.
AFM measurements were performed on a NanoScope MM-Peak Force QNM® controller equipped with a V9 MULTIMODE2-U Atomic Force Microscope from BRUKER.
In Peak Force mode, the probe and sample are intermittently brought together to contact the surface at a frequency of 2 kHz during the scan with a constant maximum force of a few tens nN maximum. Sample deformation depths are then limited to a few nanometres, minimizing the tip-sample contact area. The analysis of force curve data is done on the fly, providing a map of multiple mechanical properties that has the same resolution as the height image.
Cantilever probes RTESPA-300 model from BRUKER with a constant spring around 40 N/m are usually chosen to characterize polymers with Young's moduli comprised between 0.5 to several GPa. Each cantilever is systematically calibrated on a hard reference sample. The tip radius is estimated from scans on reference polystyrene samples with PeakForce setpoint around 20 nN. The surface moduli are calculated by DMT model (Derjaguin Muller Toporov) [20].
The samples used for AFM measurements were cut perpendicularly to fibre axis and polished up to 1 µm with diamond grinding paste and finally with alumina suspension of 0.05 µm. Residues from polishing were eliminated by successive rinsing steps and compressed air drying.

3. Results and discussion

3.1. Macro-scale mechanical characterization

The different data measured from 3 point bending test on the resin and the composite in transverse mode are reported in Table 1. Resin samples fracture could not be reached due to its important plastic behaviour. The introduction of fibres logically leads to a brittle behaviour in transverse mode with a correct load transfer considering bending modulus values increased by 2.5 compared to the bulk resin.
Data from DMA are also reported in Table 1. An important decrease of Tα is observed, associated to a decrease of the main peak area.

Table 1. Mechanical data from 3 point bending test and DMA in single cantilever mode in transverse direction.

Sample type	3 point bending test			DMA			
	E_b (MPa)	σ_R (MPa)	ε_R (%)	Tα (°C)	Area (min)	E' (MPa) 25 °C	E' (MPa) 130°C
resin	2830 (±30)	>100	>7%	93 (±1)	8,1 (±0,3)	2400 (±100)	22 (±1)
composite	6900 (±300)	87 (±11)	1,5 (±0,2)	84 (±1)	6,4 (±0,2)	7400 (±700)	170 (±20)

It shows that the introduction of fibres modifies the matrix crosslinking process. The area is proportional to relaxing species. If 8 min is measured on 100 % of matrix, for around 46 % mass fraction of matrix in the composite, the area should be around 3.5 min, below the 6.4 min measured. This can be attributed to the lower crosslinking density and/or to fibre friction.
The main α-peak can be modelled by a Gaussian peak (Fig. 1) which enables the identification of two

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relaxation peaks below and above T_α by a simple deconvolution of experimental data using ORIGIN software. These results suggest that the undercrosslinked network is heterogeneous.

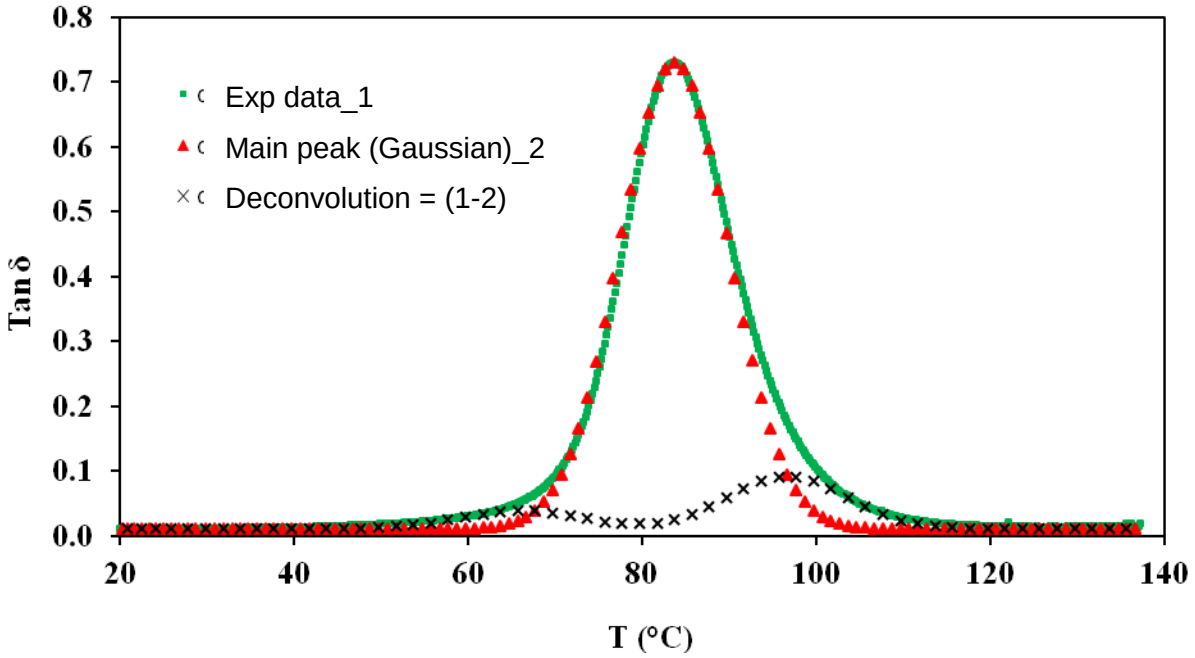

Figure 1. DMA of the composite in single cantilever mode, transverse direction

3.2. Nano-scale mechanical characterization

A modulus scan obtained in an interfacial area is represented in Fig. 2 associated to a profile along a line. A decrease (darker area) of the modulus can be observed up to 200 nm from fibre surface. This softer area defines an interphase with a undercrosslinked or plasticized network.
Below 50 nm from fibre surface, an increase of elastic modulus is observed like Gao et al. observed [4]. The values obtained within the fibre is much lower than typical values for glass fibre because the cantilever is two soft for such materials. The spring constant is adapted to polymer networks.

AFM measurements confirm the network heterogeneity suggested by Tan δ analysis. The main relaxation peak corresponds to the matrix, undercrosslinked compared to the bulk resin (-8°C for Tα). A rigid interphase at the vicinity (<50 nm) from fibre surface is characterized, followed by a softer one up to 200 nm.

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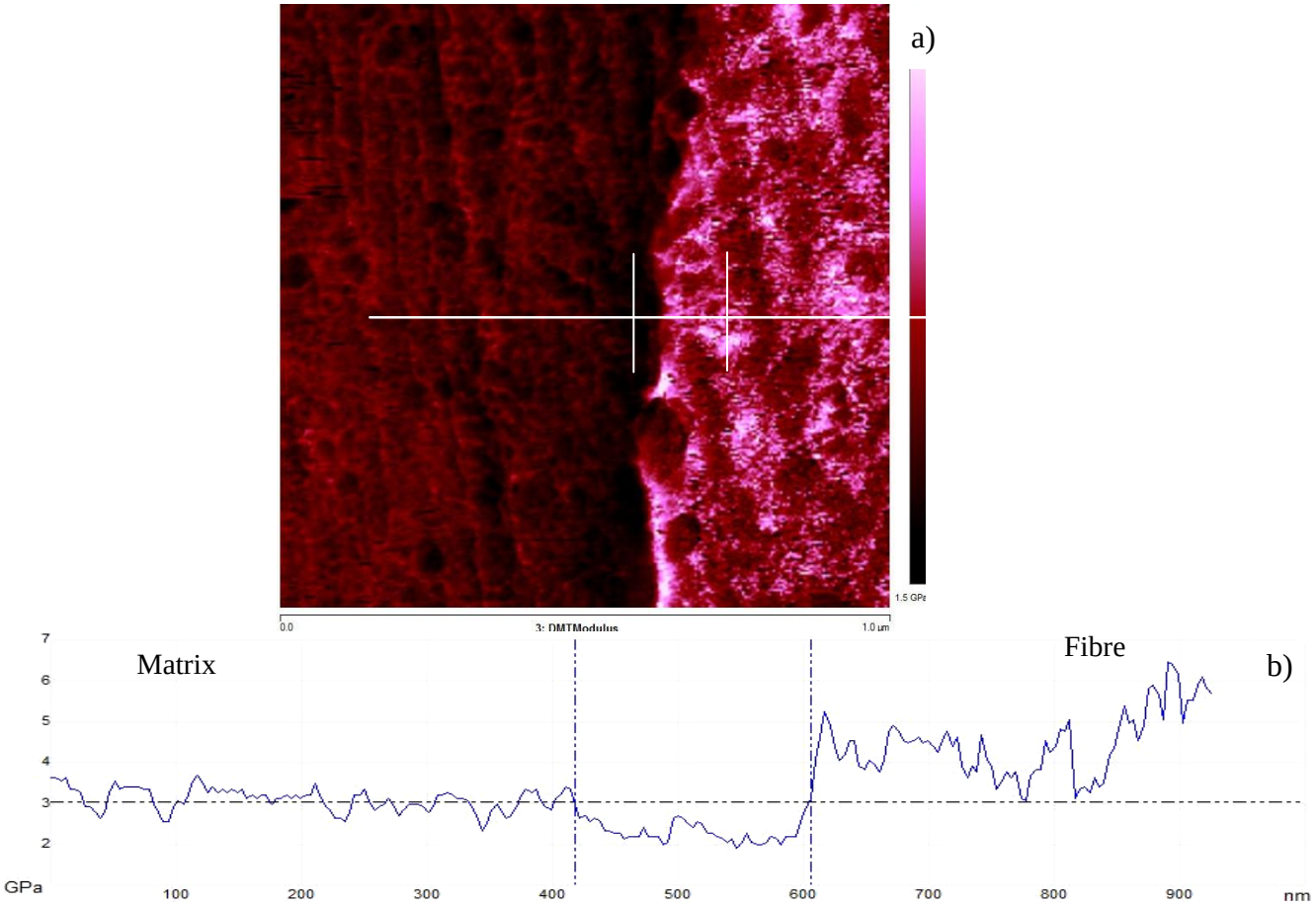

Figure 2 : a) Modulus scan (1 x 1 µm²) obtained by PeakForce QNM® b) Profile along the line

4. Conclusions

The different scales of analysis of a UD composite show up an heterogeneoux network around glass filaments. The introduction of fibres strongly modifies the matrix crosslinking process, which will influence the load transfer and more generally, the composite mechanical behaviour and durability. The high lateral resolution of AFM PeakForce mode, with very low forces applied enables the characterization of a rigid interphase, closer to the fiber, followed by a more flexible interphase which extends over hundreds of nanometers from fibre surface. These trends highlighted by other techniques are confirmed, and the method is now applied to show the influence of fibre treatments composition and proportion.

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